XIX. *On the Constitution of the Resins. Part V.* By James F. W. Johnston, *Esq., M.A., F.R.S., Professor of Chemistry and Mineralogy in the University of Durham.*

Received June 4,—Read June 18, 1840.

XVII. *Resin of Sagapenum.*

The gum resin of sagapenum has an odour very much resembling that of assafœtida, but less powerful. Like the latter gum resin, it also gives, when treated with alcohol, a pale yellow solution, while the greater portion of the mass remains undissolved. The white matter which is left behind after exhaustion with alcohol, is soluble in water, giving a milky solution.

The alcoholic solution, when evaporated, gives a pale-yellow resin, having a strong garlic odour, melting readily, and becoming fluid at 212° Fahr.

A portion of the resin prepared by evaporating the alcoholic solution at 212°, was treated for two hours with repeated portions of boiling water. The water came off colourless, but had a powerful odour of the resin, and a slightly bitter taste, leaving in the mouth an after-taste of onions. After drying it for a length of time at 212°, the resin was again dissolved in alcohol, filtered and evaporated in a thin film. It was then heated at 150° Fahr. for sixty hours, at which temperature it was still semifluid.

Burned in the air it left 0·22 per cent. of ash.

A. 8·585 grs. (8·566 grs. of pure resin) gave $\ddot{C} = 21·170$, and $\dot{H} = 6·558$ grs.

B. Further fused at 212° Fahr. for several hours, the colour became deeper yellow than before. When cold it was brittle but soft, and the particles readily cohered. In this state

10·11 grs. (10·088 grs. pure resin) gave $\ddot{C} = 25·84$, and $\dot{H} = 7·835$ grs.

These results give per cent.

	A.	B.	$C_{40}\ H_{29}\ O_9$, gives
Carbon	70·05	70·83	70·78
Hydrogen	8·51	8·63	8·38
Oxygen	21·44	20·54	20·84
	100	100	100

We may, therefore, consider the resin of sagapenum thus extracted, to be represented by $C_{40}\ H_{29}\ O_9$.

XVIII. *Resin of Galbanum.*

The galbanum resin of commerce dissolves only in small quantity in alcohol, leaving a large insoluble residue, which is principally composed of gum. Evaporated at 212° FAHR., the yellow alcoholic solution gives a beautiful brownish-yellow transparent resin, fusing readily at that temperature, and emitting the peculiar fœtid odour of this class of resins. Treated with boiling water, it imparted no colour to it.

1. After washing with boiling water, and subsequently heating for several days at 150° FAHR., it left when burned in the air 0·3 per cent. of white ash. Burned with oxide of copper,

A. 7·01 grs. (6·988 grs. pure resin) gave $\ddot{C}$ = 18·69 grs., and $\dot{H}$ = 5·21 grs.

B. After further heating, 8·08 grs. (8·055 pure resin) gave $\ddot{C}$ = 21·64, and $\dot{H}$ = 6·22 grs.

C. And 8·005 grs. (7·98 pure resin) gave $\ddot{C}$ = 21·4, and $\dot{H}$ = 6·15 grs., or per cent.,

	A.	B.	C.
Carbon	73·99	74·33	74·15
Hydrogen	8·29	8·58	8·56
Oxygen	17·82	17·09	17·29
	100	100	100

The formula $C_{40} H_{28} O_7$, gives

		Per cent.
40 Carbon	= 3057·480	74·45
28 Hydrogen	= 349·426	8·50
7 Oxygen	= 700·000	17·15
	4106·906	100

2. The close approximation between the theoretical and experimental per centage of hydrogen (in B and C) rendering this formula a little suspicious, I evaporated a second small quantity of the alcoholic solution of this resin, washed it with boiling water, and heated it long in a thin film at 200° FAHR. Of this, on analysis,

A. 6·486 grs. (6·467 grs. pure resin) gave $\ddot{C}$ = 17·13 grs., and $\dot{H}$ = 4·892 grs.

B. 7·533 grs. (7·51 grs. pure resin) gave $\ddot{C}$ = 20·17, and $\dot{H}$ = 5·72 grs., or per cent.,

	A.	B.
Carbon	73·27	74·26
Hydrogen	8·40	8·46
Oxygen	18·33	17·28
	100	100

In the first of these analyses there is, from some cause, a considerable deficiency of carbon, but the quantity of water, in regard to the accurate determination of which great pains were taken, being in both analyses less than is required by the formula

C_{40} H_{28} O_7, I think it more safe to represent the resin of galbanum by the formula C_{40} H_{27} O_7*.

$$C_{40}\,H_{27}\,O_7 \text{ gives} \begin{cases} \text{Carbon} & 74{\cdot}67 \\ \text{Hydrogen} & 8{\cdot}23 \\ \text{Oxygen} & 17{\cdot}00 \end{cases}$$
$$\overline{100}$$

The carbon by calculation is a third per cent. more than was found by experiment. But this is the direction in which errors of experiment in organic analyses are generally found, and a slight deficiency in the carbon may be expected in the case of substances which so readily fuse and give off volatile matter as this and many other of the resins. In pumping out the hygrometric moisture, some volatile vapour may also be exhausted.

3. When heated over the lamp in a platinum capsule to a temperature of about 300° FAHR., the resin above analysed gave off white fumes, and after two hours had lost nearly 10 per cent. of its weight, having become of a beautiful brownish-red colour. It still softened at 212° FAHR., and retained a little of its original odour. In this state 7·11 grs. = 7·086 pure resin, gave $\ddot{C}$ = 19·02, and $\dot{H}$ = 5·18, or per cent.,

Carbon	74·22	40 atoms.
Hydrogen	8·12	26·7 atoms.
Oxygen	17·66	7·27 atoms.
	100	

In this result we see an apparent approximation to the formula C_{40} H_{26} O_7, the hydrogen decreasing, while the oxygen appears to increase.

In the former of this series of papers (Part IV.), I gave the analysis of the resins of ammoniac, opoponax, and assafœtida, which together with those of sagapenum and galbanum, constitute the group of fœtid resins of some chemists†. The odour of the last four of these resins is very similar, though that of assafœtida is the most powerful and disagreeable. We might anticipate, therefore, some resemblance in constitution among these resins, since they exhibit in common this very striking property. In the *irrational* formulæ above obtained, however, we do not recognize any close resemblance, either in the proportions of hydrogen or of oxygen which they contain. Thus the

Resin of ammoniac = C_{40} H_{25} O_9
Resin of opoponax = C_{40} H_{25} O_{14}
Resin of assafœtida = C_{40} H_{26} O_{10}
Resin of galbanum = C_{40} H_{27} O_7
Resin of sagapenum = C_{40} H_{29} O_9.

* See under elemi resin B.

† THOMSON's Organic Chemistry (1838), p. 567.

Still it appears to me exceedingly probable, that in the *rational* formulæ for this and similar groups of resins exhibiting striking sensible properties, common to all, we may hereafter find that connexion in constitution which the *irrational* formulæ do not exhibit, and the absence of such connexion is not without its weight in favour of the opinion, that the resins in general are not mere oxides of a carbo-hydrogen radical, but are *in many cases* at least made up of two or more compound radicals. Into the consideration or development of this view, I do not propose to enter, until, in the sequel of the present and in some subsequent papers, I shall have brought forward facts and analytical results by which it may be better sustained.

XIX. *Euphorbium Resin.*

This resin occurs in commerce in the form of tears, generally enveloping small twigs or thorns of the shrub from which it had exuded. It is largely mixed with seeds and spines, and sometimes with at least three-fourths of its weight of clay and other earthy matters. It is of a pale-yellow colour, and is distinguished by its peculiarly hot and acrid taste, and its stimulating action on the organs of smell and even externally upon the skin.

When digested in cold alcohol (0·8) a pale-yellow solution is obtained, which by evaporation gives a yellow resin. After being treated with cold alcohol as long as anything is taken up, a large insoluble residue remains. Boiled in alcohol, this residue yields a solution, from which, on cooling, a white resinous substance is deposited in a crystalline form. This sparingly soluble resin has been examined and analysed by Rose. To the results of these analyses I shall presently have occasion to advert.

I. *Resin* A. *of Euphorbium* (*readily soluble in cold alcohol*).

1. When the native tears of euphorbium are digested in cold alcohol, a pale-yellow solution is obtained, and from this by evaporation, a brownish-yellow resin, readily fusing at 212°. If this resin be treated with boiling water, the first portion of the liquid employed acquires a pale-yellow tinge, and a small quantity of oil is removed. By subsequent washing nothing further appears to be taken up by the water. Separated from the water, the resin is pale-yellow and opake, like common Burgundy pitch, and requires long drying at 212° in a thin film to render it perfectly dry and transparent. It is now less fusible, though it still becomes semifluid at 212°, and when cold is brittle, in mass of a brownish red colour, and in fragments exceedingly electric.

In this state, when burned in the air, 5·605 grs. left 0·075, or 1·34 per cent. of ash; and with oxide of copper,

A. 9·1 grs. (8·978 grs. pure resin) gave $\ddot{C} = 24·39$, and $\dot{H} = 7·91$ grs.

B. 7·19 grs. (7·094 grs. pure resin) gave $\ddot{C} = 19·29$, and $\dot{H} = 6·3$ grs.

These are equivalent to

	A.	B.	$C_{40}H_{31}O_6$ gives
Carbon	75·12	75·21	75·59
Hydrogen	9·79	9·87	9·56
Oxygen	15·09	14·92	14·85
	100	100	100

2. The same portion of crude euphorbium being treated with a second quantity of cold alcohol, gave a solution from which the resin was obtained as above described, washed with water and dried at 212° FAHR. When burned in the air it left 1 per cent. of ash.

A. 7·71 grs. (7·61 grs. pure resin) gave $\ddot{C}=21·0$, and $\dot{H}=7·03$ grs.
B. 8·19 grs. (8·075 grs. pure resin) gave $\ddot{C}=22·28$, and $\dot{H}=7·38$ grs.; or per cent.,

	A.	B.	
Carbon	76·29	76·30	40 atoms.
Hydrogen	10·26	10·15	32·6 atoms.
Oxygen	13·45	13·55	5·43 atoms.
	100	100	

The difference between the results obtained from this and from the former portion, may be ascribed either to a difference in the mode of heating the two portions, the latter after drying at 212° FAHR. having been further fused at a slightly elevated temperature, when bubbles of volatile matter began to show themselves; or to an admixture of the less soluble resin (B.) contained in the euphorbium of commerce, which according to the analysis of ROSE, contains more hydrogen and less oxygen than are present in the more soluble resin (A.). At all events the fractional atom of oxygen exhibited by the results of these second analyses, shows that the portion analysed is not to be considered as a pure resin.

3. To determine this point the crude resin was treated with a third portion of cold alcohol, and the solution, which was much paler in colour and less concentrated than either of the former, was submitted to evaporation. As the alcohol was drawn off, the solution became milky, and gradually deposited a portion of a white powder, which was the second resin of euphorbium. This resin, therefore, is soluble to some extent in cold alcohol, and is consequently capable of being taken up along with the more soluble resin, and in greater quantity, of course, by the second than by the first portion of alcohol with which the tears may be treated.

The remainder of the second portion which had been analysed, when treated with a small quantity of alcohol, readily dissolved, with the exception of a slight residue, which resembled the powder of the second resin. It is not unlikely, therefore, that even the resin employed in the first series of analyses might contain a little of resin B, by which the carbon and hydrogen would be slightly increased. The formula $C_{40}H_{31}O_6$ deduced from them, though agreeing very closely with the experimental

results, must still be considered as open to suspicion, and be regarded only in the light of an approximation. The same remark applies also to the resin A. of elemi, though to a less extent, since the resin B. of elemi is less soluble than resin B. of euphorbium.

II. *Resin* B. *of Euphorbium.*

This resin has also been analysed by ROSE, who obtained

Carbon	81·47	81·70	40 atoms.
Hydrogen	11·33	11·36	34·6 atoms.
Oxygen	7·20	6·94	2·5 atoms*.
	100	100	

ROSE thinks it probable that the resin he analysed was not quite pure, which is rendered very probable by his results not agreeing with any formula of which C_{40} is a member. I have not hitherto obtained it in sufficient quantity to enable me to repeat his analysis; when I shall hereafter describe the results of experiments on the relation of the resin A. to certain powerful reagents, I hope to have an opportunity of again adverting to the constitution of resin B. of euphorbium.

This resin is considered by ROSE to be probably isomeric with the resin B. of elemi, but the difference in their physical characters and solubility, supposing no reliance to be placed on the analyses, appear sufficient to render that opinion very doubtful.

XX. *Elemi Resin.*

The elemi resin of commerce, like that of euphorbium, consists of two resins, one readily soluble in cold alcohol, the other dissolving, to any extent, only in boiling alcohol, and falling again in great measure as the liquid cools. The soluble resin has the ordinary resinous aspect, is transparent, brittle, brownish yellow, and forms salts with the bases; the sparingly soluble resin falls in colourless crystals, which melt at 300° + FAHR. into a colourless fluid, becoming when cold a nearly colourless brittle mass with a resinous fracture, the solution of which does not precipitate bases.

The crystallized resin has been analysed by ROSE, HESSE, and MARCHAND, and its composition determined with considerable accuracy, and I have thought it necessary to submit it to a further examination, chiefly for the purpose of comparing my results with those obtained by these distinguished chemists.

I. *Resin* A. *of Elemi* (*readily soluble in cold Alcohol*).

Reduced to powder and digested with cold alcohol, the crude elemi resin gives a yellow solution, which by evaporation yields a yellow resin. When nearly free from alcohol this resin emits a strong odour of oil of lemons. Treated with boiling

* POGGENDORFF's Annalen, xxxiii. p. 53.

water it loses its transparency and becomes white and opake, but imparts no colouring matter to the water. Thus prepared and long dried at 212° Fahr., it left when burned in the air 0·10 per cent. of ash.

A. 8·31 grs. (8·302 grs. pure resin) gave $\ddot{C} = 23{\cdot}7$, and $\dot{H} = 7{\cdot}9$ grs.
B. 8·04 grs. (8·032 grs. pure resin) gave $\ddot{C} = 22{\cdot}71$, and $\dot{H} = 7{\cdot}45$ grs.
C. 7·465 grs. (7·458 grs. pure resin) gave $\ddot{C} = 21{\cdot}26$, and $\dot{H} = 6{\cdot}998$ grs.

	A.	B.	C.	$C_{40}H_{32}O_4$ gives
Carbon	78·93	78·15	78·82	79·275
Hydrogen	10·57	10·30	10·43	10·355
Oxygen	10·50	11·55	10·75	10·370
	100	100	100	100

II. *Resin* B. *of Elemi* (*very sparingly soluble in cold, more largely in boiling Alcohol, out of which it crystallizes on cooling*).

This resin remains in the form of a white powder when the natural elemi resin is exhausted with cold alcohol, as long as a coloured solution is obtained. This white powder dissolves in boiling alcohol, and yields the pure resin in the state of minute white crystals as the solution cools. The constitution of this resin appears to be pretty well established, having been analysed by Hesse, Rose, and Marchand, with results which are very closely accordant.

The specimen I analysed, after drying between folds of bibulous paper, had been long heated at 200° Fahr., and was then in the state of a white powder.

A. 6·893 grs. gave $\ddot{C} = 21{\cdot}265$ grs., and $\dot{H} = 7{\cdot}395$ grs.
B. 6·76 grs. gave $\ddot{C} = 20{\cdot}78$ grs., and $\dot{H} = 7{\cdot}2$ grs.

These results compared with those of the other experimenters, give per cent.

	Hesse.		Rose.		Marchand.		Johnston.	
Carbon	85·36	85·06	85·11	85·61	85·54	85·59	85·30	85·00
Hydrogen	11·51	11·54	11·79	11·83	11·61	11·59	11·92	11·83
Oxygen	3·13	3·40	3·10	2·56	2·85	2·82	2·88	3·17
	100	100	100	100	100	100	100	100

The only difference of any consequence among these analyses is in the amount of hydrogen. I have given only two of the results published by each of the above chemists, but in three others published by Rose, the hydrogen amounted to 11·85, 11·89, 11·98 respectively. Finding the quantity of hydrogen deduced from my first analysis to be so high, I used greater precautions in pumping out the hygrometric moisture in the second, but without bringing it much nearer the results of Hesse or Marchand. Still the formula adopted by Hesse is that which must be adopted as the most probable, if any allowance is to be made in the analyses of Marchand, Rose, and my-

self for an error of hydrogen in excess. Thus

	HESSE's formula $C_{40} H_{33} O_1$ gives	while $C_{40} H_{34} O_1$ gives
Carbon	85·66	85·36
Hydrogen	11·53	11·85
Oxygen	2·81	2·79
	100	100

The quantity of hydrogen, 11·85, in the second column is greater than the minimum of water either in ROSE's analyses or mine, and therefore according to the principle adopted in deducing all the formulæ exhibited in the present series of papers, $C_{40} H_{33} O_1$ is that which these analyses indicate as the most probable. It is chiefly, I believe, to the hygrometric state of the oxide of copper, that analyses performed according to *the method of* LIEBIG and with equal care, differ slightly in the amount of hydrogen. If the oxide be newly prepared by calcining the nitrate, and be therefore in a minute state of division, it appears almost impossible, *as a general result*, to free it so completely from moisture that the hydrogen shall not be 0·2 to 0·3 per cent. in excess, while the same experimenter will come within 0·1 or 0·15 per cent. by the use of oxide of copper, which has been frequently heated to redness, and after having been used for analysis, has been repeatedly re-oxidized by heating in a current of air.

XXI. *Resin of Bdellium.*

The resin of bdellium occurs in commerce, in translucent yellow rounded masses, often of considerable size. The masses vary in tint, as is the case with many other resins, some of them being of a brown colour, more or less dark.

A single yellow mass, about half an inch in diameter, was reduced to powder and digested in cold alcohol. A pale yellow solution was obtained, from which, by evaporation in a thin film, a yellow resin was obtained. It was treated with successive portions of boiling distilled water, of which only the first portion acquired a slightly yellow tinge. By this treatment it scarcely lost its transparency, differing in this respect very much from the soluble resins of euphorbium and elemi above-described. The resin was then dried for forty-eight hours at 180° FAHR. in the state of a thin film. It now formed a beautiful transparent yellow resin, softening readily at 212°, and at that temperature emitting a slightly fragrant resinous odour. Burned in the air it left 0·17 per cent of ash.

A. 7·29 grs. (7·277 grs. pure resin) gave $\ddot{C} = 20·15$, and $\dot{H} = 6·54$ grs.

B. 7·185 grs. (7·172 grs. pure resin) gave $\ddot{C} = 19·77$.

C. Another lump was treated in a similar manner, and the resin similarly dried. Of this

7·687 grs. (7·673 grs. pure resin) gave $\ddot{C} = 21·13$, and $\dot{H} = 6·97$ grs.

D. Of the alcoholic solution of the resin from the same lump, another portion was

evaporated separately and much longer heated, when 6·44 grs. (6·429 grs. pure resin) gave $\ddot{C} = 17·97$, and $\dot{H} = 5·715$ grs.

These results give per cent.,

	A.	B.	C.	D.
Carbon	76·57	76·22	76·15	77·29
Hydrogen	9·98		10·09	9·87
Oxygen	13·45		13·76	12·84
	100		100	100

The result of analysis D. agrees very closely with the formula $C_{40}\ H_{31}\ O_5$, which gives

		Per cent.
40 Carbon	= 3057·480	77·51
31 Hydrogen	= 386·867	9·81
5 Oxygen	= 500·000	12·68
	3944·347	100

I consider the portion last analysed (D.) to have been most nearly in the normal state, and the result obtained to be the more trustworthy, from the near approximation to the calculated numbers above given. It would appear, therefore, that the different lumps of the natural resin of bdellium, as it is met with in commerce, contain the same resinous substance, and that after extraction by alcohol and repeated washing with boiling water, this resin requires prolonged heating at a temperature of 200° FAHR. in the state of a thin film, to free it from water and other volatile matters, and bring it to its normal state.

The formula $C_{40}\ H_{31}\ O_5$ is that assigned in the third part of these researches* to the resin A. of sandarach, which differs from that of bdellium, however, in being a sparingly soluble resin. Whether these resins be really isomeric, or whether they differ by an atom of hydrogen more or less, will be investigated in a future paper.

The insoluble matter which remains after the natural resin of bdellium is exhausted with cold alcohol, consists only of gum, and is taken up by boiling water.

XXII. *Resin of Benzoin.*

The resin of benzoin is one to which considerable interest attaches from its connexion with benzoic acid, and the numerous series of remarkable compounds, to the knowledge of which the study of that acid has led. I commenced the study of it, therefore, with the hope, not merely of elucidating its relation to the other resins, but also of throwing some light upon that which it bears, or may be expected to bear, to the acid so readily obtained from it. In the latter expectation, however, I have for the present been in some measure disappointed, in so far at least as I have failed to obtain a formula for this resin, by which its rational connexion with the radical benzyle, and its derivatives, can be, if not satisfactorily comprehended, at least numeri-

* Philosophical Transactions, 1839, p. 294.

cally stated. The investigation of this resin indeed has presented many difficulties, chiefly, as it appears to me, from the ease with which it undergoes a partial decomposition even at very moderate temperatures. I have made numerous analyses of it, in various states, with the view, if possible, of establishing a formula for it in the normal state, and, amid the many changes it undergoes, of arriving at a process by which it may always be obtained of uniform composition. How far this end has been attained the following experiments will show.

The resin of benzoin, as it occurs in commerce, consists of brown opake brittle masses, containing here and there small pieces of a yellowish white colour and semi-transparent. These latter portions melt at about 200° FAHR. into a transparent nearly colourless resin, which on cooling becomes brittle. At a higher temperature it gives off water and benzoic acid, and becomes brown.

1. Of this pure white variety a portion was dissolved in alcohol, evaporated and heated in a thin film at 212° FAHR. till it ceased *sensibly* to evolve benzoic acid. During this heating it gradually assumed a brownish tinge. In this state, when burned in the air, it left 0·29 per cent. of ash.

7·64 grs. (7·618 grs. pure resin) gave $\ddot{C} = 19·60$, and $\dot{H} = 6·84$ grs.

2. The colourless resin in its natural state, without being dissolved, was kept for twenty hours in a semifused state at 200° FAHR. It left, when burned in the air, 0·24 per cent. of ash, and

9·87 grs. (9·847 grs. pure resin) gave $\ddot{C} = 26$ grs., and $\dot{H} = 5·907$ grs.

3. The same natural resin was dissolved in alcohol, evaporated, subsequently treated with repeated portions of boiling water, which dissolved out benzoic acid, and then dried at 212° FAHR. It left 0·23 per cent. of ash, and

8·21 grs. (8·192 grs. pure resin) gave $\ddot{C} = 21·76$, and $\dot{H} = 5·23$ grs.

4. The natural mixture of brown and white resins was boiled repeatedly in water, twice with dilute solutions of carbonate of soda, with the view of extracting all the benzoic acid, and again in water to separate the soda. It was then dissolved in alcohol, evaporated and dried at 212° FAHR. It left 0·3 per cent. of ash.

11·46 (11·426 grs. pure resin) gave $\ddot{C} = 29·73$, and $\dot{H} = 7·363$ grs.

5. A portion of the resin thus treated (4.) was again boiled in a concentrated solution of carbonate of potash, washed with a dilute solution of muriatic acid, and afterwards boiled in acetic acid and well washed with water. It still retained some potash, for when burned in the air it left 1·03 per cent. of ash, being 0·73 of carbonate of potash, and the usual 0·3 per cent. of earthy matter. This quantity of carbonate of potash retained 0·26 per cent. of carbonic acid, the potash and earthy matter being together 0·77 per cent. The resin was of a reddish-brown colour, and was soluble without residue in both alcohol and ether, though, according to UNVERDORBEN*, boiling with carbonate of potash converts benzoin into two resins, one soluble and

* THOMSON's Organic Chemistry (1838), p. 542.

the other insoluble in ether. This change, however, I am satisfied must, in UNVERDORBEN's experiment, have proceeded from some other cause than simple boiling in carbonate of potash. It may possibly have been due to the action of caustic alkali contained in his carbonate, which, as I shall hereafter have occasion to show, exercises an important modifying power over this resin at a boiling temperature, converting it into at least two resins of very different composition; or the manner of heating, or length of time during which it was boiled, may have led him to a result different from that which I have obtained. In the case of substances so susceptible of metamorphoses, as the resins will hereafter appear to be, we ought to hesitate in ascribing to errors of observation, a difference in results which may have arisen only from a slight difference in the circumstances under which the experiments, made by different chemists, were conducted. The benefit of this observation is especially due to UNVERDORBEN, who did so much, considering the state of chemistry in his time, to throw light on this interesting family of organic products.

Thus boiled in carbonate of potash,

A. 8·945 grs. (8·876 grs. pure resin) gave $\ddot{C} = 23{\cdot}22$, and $\dot{H} = 5{\cdot}95$ grs.

B. 9·905 grs. (9·829 grs. pure resin) gave $\ddot{C} = 25{\cdot}905$, and $\dot{H} = 6{\cdot}66$ grs.

The entire results above-detailed, allowing for the earthy matter and for the carbonate of potash, present in these last, give per cent.,

Dissolved in alcohol and heated to 212° FAHR.	Native resin heated long at 200° FAHR.	Dissolved in alcohol and treated with boiling water.	Boiled in water and in dilute carbonate of soda.	Boiled in concentrated carbonate of potash.	
				A.	B.
1.	2.	3.	4.	5.	6.
Carbon 71·14	73·06	73·43	71·95	72·59	73·13
Hydrogen 6·84	6·67	7·09	7·16	7·45	7·53
Oxygen 22·02	20·27	19·48	20·89	19·96	19·34
100	100	100	100	100	100

These results are very discordant, and on such of them as have not been repeated, perhaps much reliance ought not to be placed. There is so far an agreement among them, however, that the per centage of hydrogen goes on increasing with every successive operation to which the resin is subjected. This is quite in accordance with what ought to take place, if we suppose that additional portions of benzoic acid are removed at each step. Anhydrous benzoic acid consists of $C_{14}\ H_5\ O_3$, or calculated to C_{40}, for the purpose of comparison, it is $C_{40}\ H_{14{\cdot}3}\ O_{8{\cdot}57}$. In this latter formula, while the oxygen is slightly in excess, the hydrogen is many atoms less than in the resin in any of its states. The extraction of benzoic acid from the resin, must therefore necessarily increase the proportion of hydrogen in what remains, while, with the aid of the water evolved at the same time, the oxygen will be to a certain extent diminished. The resin analysed after boiling in dilute carbonate of soda (4.) still gave off benzoic acid and water, when heated in a close tube, while after further boiling in concentrated carbonate of potash it gave no sensible quantity of crystals (analyses

5. and 6.). We are to suppose, therefore, that, whether they actually existed as such in the resin or were formed by the action of the alkali, an additional quantity of benzoic acid and water was removed from the resin by the carbonate of potash. With this, the formulæ deduced from analyses 4, 5 and 6 agree, being respectively $C_{40}\,H_{24}\,O_9$, and $C_{40}\,H_{24}\,O_8$. Thus

	$C_{40}\,H_{24}\,O_9$ gives	Found by analysis 4.	$C_{40}\,H_{24}\,O_8$ gives	Found by analyses 5 and 6.	
Carbon	71·82	71·95	73·55	72·59	73·13
Hydrogen	7·03	7·16	7·25	7·45	7·53
Oxygen	21·15	20·89	19·20	19·96	19·34
	100	100	100	100	100

Without laying much stress at present on the first of these formulæ, we may from the above analyses conclude, that the benzoin of commerce, and after partial heating and boiling in water, is of very variable composition, but that after boiling in concentrated solutions of the carbonated alkalies and carefully heating, its constitution may be represented very approximately by $C_{40}\,H_{24}\,O_8$. This conclusion is confirmed by the examination of the resin which remains after the crude benzoin is boiled with quicklime.

II. *Action of Caustic Lime on Resin of Benzoin.*

When the benzoin resin of commerce is intimately mixed with quicklime and boiled in a large quantity of water, the resin unites with the lime, and forms a nearly insoluble compound of a beautiful purple colour, while benzoate of lime is also produced and dissolved by the boiling water. Thrown on the filter and washed for a length of time, the washings pass through of a yellow colour, which diminishes little in intensity, and is due chiefly to the solubility of the compound of a peculiar resin with the lime. I have subjected three successive portions of the crude resin to this treatment, and though I place most reliance on the results of the last portion, I insert the analyses of the other portions, as they are not without interest, in connexion both with the nature of the resin itself, and the precautions necessary to be adopted in order to obtain it of constant composition.

1. After boiling with quicklime and washing with boiling water, the purple compound was decomposed by boiling with dilute muriatic acid, and afterwards with water. It was then dried at 212° Fahr., treated with cold alcohol, and the solution evaporated at 212° Fahr. The resin was of a reddish-brown colour, and left 0·7 per cent. of ash.

8·48 grs. (8·42 grs. pure resin) gave $\ddot{C} = 21{\cdot}61$, and $\dot{H} = 5{\cdot}595$ grs.

2. The second portion similarly treated gave a similar resin, which left, when burned in the air, 0·69 per cent. of ash, and of which when heated long at 212° Fahr.

A. 8·00 grs. (7·945 grs. pure resin) gave $\ddot{C} = 20{\cdot}47$, and $\dot{H} = 5{\cdot}176$ grs.

B. Heated four days longer at 180° Fahr., 8·96 grs. (8·898 grs. pure resin) gave $\ddot{C} = 23{\cdot}21$, and $\dot{H} = 5{\cdot}61$ grs.

3. The above results not being satisfactory, I prepared a larger quantity of the resin. Twelve hundred grains were boiled in an iron kettle with a large quantity of slaked lime in fine powder, in repeated portions of water, till ten or twelve quarts had passed through the filter. The solution was pale yellow to the last, muriatic acid threw down from it a resin in white flocks, which in the last solutions was smaller in quantity. This precipitate was collected for subsequent examination.

The compound with lime was, as before, of a purple colour, which became more bright and beautiful as the excess of lime was gradually removed by digestion with dilute muriatic acid. When completely decomposed by this acid, a yellow solution and a gray resinous powder were obtained. The powder was well washed, dried at 212° Fahr., and then treated with alcohol. What remained undissolved was chiefly sand and earthy matter. The alcoholic solution, evaporated and dried in a thin film at 150° Fahr., gave a resin which, after heating several hours at 212° Fahr., left 0·904 per cent. of ash, and

A. 7·36 grs. (7·29 grs. pure resin) gave $\ddot{C}$ = 18·69, and $\dot{H}$ = 4·83 grs.

B. Heated further for several hours at 220° Fahr., 8·59 grs. (8·512 grs. pure resin) gave $\ddot{C}$ = 22·49, and $\dot{H}$ = 5·695 grs.

C. Further heated for twelve hours at 180° Fahr., 6·94 grs. (6·875 grs. pure resin) gave $\ddot{C}$ = 18·21, and $\dot{H}$ = 4·725 grs.

D. Again heated to incipient fusion (300 ± Fahr.), when the particles began to cohere, 7·53 grs. (7·46 grs. pure resin) gave $\ddot{C}$ = 19·735, and $\dot{H}$ = 4·925 grs.

The following Table shows the result of these analyses of the three several portions of resin prepared by boiling with quicklime:—

First portion dried at 212°.	Second portion.		Third portion.			
	Heated at 212°.	Longer at 180° Fahr.	Heated at 212°.	Further at 220° Fahr.	Further 12 hours at 180° Fahr.	Further to incipient fusion (300° ?).
7.	8.	9	10.	11.	12.	13.
Carbon 70·97	71·24	72·13	70·89	73·07	73·26	73·15
Hydrogen 7·38	7·24	7·01	7·36	7·43	7·63	7·34
Oxygen 21·65	21·52	20·86	21·75	19·50	19·11	19·51
100	100	100	100	100	100	100

The identity of the last three results entitles us to place reliance upon them, as indicating very approximately the constitution of the resin in its normal (?) state. Comparing these with the results obtained by the analyses 5 and 6 previously given, we see that the effect of prolonged boiling with quicklime is to bring the resin into the same state as when it is boiled with concentrated carbonate of soda. In the latter analyses, however, the experimental came still nearer to the calculated numbers given by the formula $C_{40}\ H_{24}\ O_8$. Analysis 13 was undertaken in consequence of the discordance as to the amount of hydrogen between 11 and 12, and from the precautions taken,

the result of this analysis may be considered to approach very near to the true quantity.

On comparing together the columns 7, 8, 9 and 10, we see that by prolonged heating some volatile matter is given off, by which the per centage of carbon is increased; and that such is the case, appears more clearly if a portion of the resin after prolonged heating at 200° FAHR. be further heated in a close tube 50° to 100° higher. In the cooler part of the tube a colourless naphthoid fluid gradually condenses, *while the resin does not even begin to cohere.* It is difficult to pronounce with certainty that the resin is actually decomposed at this temperature, though it does seem exceedingly probable. And if we consider the coincidence of the analyses 7, 8 and 10, (the results of which are nearly identical, and for all of which the several portions of resin were heated only to 212° FAHR.,) to indicate a probable constancy of composition at this temperature, and that at a higher heat it undergoes decomposition, we should be led to adopt a formula containing nine of oxygen as representing the constitution of this resin of benzoin in its *real* normal state. Thus the formula $C_{40}\ H_{24}\ O_9$ gives

Carbon	71·82
Hydrogen	7·03
Oxygen	21·15
	100

and these numbers so far agree with the results 7, 8, 9 and 10, as to render this formula exceedingly probable. On the whole, therefore, as the best expression of the entire results, I am inclined to consider

A. That the resin obtained when the benzoin of the shops is boiled with quicklime, well washed, as above described, separated by muriatic acid, extracted by alcohol, and dried in a thin film at 212° FAHR., is represented very nearly by the formula $C_{40}\ H_{24}\ O_9$*.

B. That when this resin is further heated to incipient fusion, or for a length of time at a temperature approaching that at which it melts, it gives off a volatile liquid, and acquires the composition represented by the formula $C_{40}\ H_{24}\ O_8$.

4. It has been stated above, that when the compound of the resin of benzoin with lime was washed with boiling water, a yellow solution was obtained, which on being treated with muriatic acid gave a resinous precipitate in gray flocks. This was collected, washed, and dried at 212° FAHR. The quantity was very small, only about fourteen grains being obtained from 1200 employed in the last experiment. Dissolved in alcohol and evaporated in a thin film, it was reddish-brown, and had much the appearance of the resin already analysed. Burned in the air it left 0·6 per cent. of ash, and after being heated long at 180° FAHR., and afterwards to incipient fusion, when it gave off a perceptible quantity of a volatile oil,

6·87 grs. (6.835 grs. pure resin) gave $\ddot{C}$ = 18·33, and $\dot{H}$ = 5·67 grs., or per cent.,

* By referring to p. 371, it will be seen that the results of the fourth analysis agree with this formula also.

	(14.)	$C_{40} H_{29} O_7$ gives	$C_{40} H_{30} O_7$ gives
Carbon	74·11	74·22	73·99
Hydrogen	9·21	8·78	9·07
Oxygen	16·68	17·00	16·94
	100	100	100

Whichever of the two formulæ in the second and third columns we adopt as the representative of the constitution of this resin, we find it very different from that of the resin of benzoin in any of the states in which we have hitherto had occasion to examine it. If we suppose it to be most nearly represented by $C_{40} H_{30} O_7$, we find that by the action of quicklime on the natural resin of benzoin there is separated *or formed* a small portion of a resin containing so much hydrogen as to place it *irrationally* in our artificial group, of which $C_{40} H_{32 \pm x} O_y$ is the expression, and colophony the type. Are we, therefore, to infer that the natural resin is a mixture or compound of benzoic acid, of a resin $C_{40} H_{24} O_8$, and of another $C_{40} H_{30} O_7$, and that quicklime and carbonated alkalies are capable of separating these from each other; or that by these agents the resin is decomposed and *transformed* into these three compounds, which by their means are capable of being obtained from it? This question we shall be better able to consider when we have examined the action of other agents on the natural resin.

III. *Action of Caustic Potash on Resin of Benzoin.*

When to the solution obtained by digesting the resin of commerce in cold alcohol, a concentrated aqueous solution of caustic potash is added, a gray precipitate falls, and the supernatant liquid becomes much darker in colour. If the alkali be added drop by drop as long as any precipitate appears, the two resinous salts may be separated from each other with considerable accuracy, but if it be added in excess the precipitate readily dissolves. In this case the precipitate is again obtained by adding a fresh portion of the alcoholic solution of the resin.

1. The resinous salt thus thrown down was washed with boiling water, in which it is nearly insoluble, afterwards re-dissolved in dilute caustic potash, precipitated by dilute muriatic acid, which separated the alkali, and then washed with copious affusions of hot water. The resin was thus obtained in the form of a gray powder, which, when dry, dissolved in large quantity and without appreciable residue in hot alcohol and ether, but, from both solutions, fell in large quantity on cooling.

A. Alcohol in small quantity was digested on the whole of the resin, and the solution evaporated in a thin film, when it left in the air 1·03 per cent. of ash.

6·43 grs. (6·364 grs. pure resin) gave $\ddot{C} = 16·74$, and $\dot{H} = 4·293$ grs.

B. A second portion of alcohol gave a solution, the resin obtained from which, after long heating at 150° FAHR., left 0·81 per cent. of ash, and

5·71 grs. (5·66 grs. pure resin) gave $\ddot{C} = 14·615$, and $\dot{H} = 3·66$ grs.

C. Ether now digested on the mass, already treated with alcohol, gave a resin which, after long heating at 180° Fahr., left 0·39 per cent. of ash, and

5·85 grs. (5·827 grs. pure resin) gave $\ddot{C} = 15{\cdot}17$, and $\dot{H} = 3{\cdot}575$ grs.

D. Ether was again digested on the residual resin, the solution evaporated, and the film long heated at 250° Fahr.

5·77 grs. (5·75 grs. pure resin) gave $\ddot{C} = 15{\cdot}01$, and $\dot{H} = 3{\cdot}48$ grs.

These several results are equivalent to

	By alcohol.		By ether.	
	A (15).	B (16).	C (17).	D (18).
Carbon	72·73	71·39	71·99	72·18
Hydrogen	7·49	7·18	6·82	6·72
Oxygen	19·78	21·43	21·19	21·10
	100	100	100	100

These analyses show that the mass thus treated successively with alcohol and ether, was a mixture of at least two resins, of which the more soluble was the first taken up, and contained most hydrogen. The results of analysis A. agree very nearly with those obtained for the resin $C_{40}\ H_{24}\ O_8$, produced by the action of quicklime on the crude resin, and the portion first taken up by the alcohol may have consisted chiefly of that resin. Analysis B. again, coincides very closely with the formula $C_{40}\ H_{24}\ O_9$, which we have also formerly obtained. But these coincidences may be accidental, and it is the successive portions taken up by the ether, which give analogous results, that we are to consider as approaching nearest to the resin in its probably normal state. These results agree with the formula $C_{40}\ H_{22}\ O_9$, which gives

	Calculated.	Found (17.)	(18.)
Carbon	72·24	71·99	72·18
Hydrogen	6·48	6·82	6·72
Oxygen	21·28	21·19	21·10
	100	100	100

Besides the admixture of the resin $C_{40}\ H_{24}\ O_8$ above supposed, there may have been present in the mass, a portion also of the resin about to be described.

2. The alcoholic solution which remained after precipitating the crude resin as above described, was diluted with water, by which only a small quantity of resin was precipitated. The filtered solution was then decomposed by excess of muriatic acid, and the precipitated resin well washed with copious affusions of hot water, by which the resinous powder was not melted or made to cohere. It was then collected on the filter, dried at 212° Fahr., dissolved in alcohol, filtered, and again evaporated, and dried at a gentle heat. It left 0·2 per cent. of ash.

Four several portions of the *same* alcoholic solution were thus evaporated and analysed in succession:—

A. 7·575 grs. of pure resin, gave $\ddot{C}$ = 20·28 grs., and $\dot{H}$ = 6·245 grs.

B. 7·475 grs. of pure resin, heated at 200° FAHR. for a longer period, gave $\ddot{C}$ = 19·76 grs., and $\dot{H}$ = 6·09 grs.

C. 7·166 grs. of pure resin still longer heated, gave $\ddot{C}$ = 18·30, and $\dot{H}$ = 5·705 grs.

D. 7·325 grs. of pure resin, heated twenty-four hours longer than C., gave $\ddot{C}$ = 19·02, and $\dot{H}$ = 6·073 grs., or per cent.,

	A (19).	B (20).	C (21).	D (22).
Carbon	74·03	73·09	70·61	71·80
Hydrogen	9·16	9·05	8·84	9·21
Oxygen	16·81	17·86	20·55	18·99
	100	100	100	100

Though longer heated, the portion D. had not been so much changed as the portion C. There is no question of comparative purity in this instance, since all the portions were obtained from the *same* solution. The differences, if not errors of analysis, are due to the action of heat alone, and the discordant results serve to show how very much a resin may be changed by prolonged heating, at a temperature far below that at which it melts, which in the present case was never approached.

If we compare the result A. with the constitution of the small quantity of the second resin obtained by the action of quicklime (p. 375, analysis 14.), we find them to be nearly identical; and as the resin of analysis A. (19.) had been long heated at 200° FAHR., I am inclined to think that first portion to have been most nearly in the normal state of the resin, and that the differences observed in the constitution of the other portions are due to the evolution in greater or less quantity of that volatile oily product, which I have already described as given off when the resin of analysis 14 was heated to a temperature approaching that at which it began to cohere.

From this imperfect examination of the action of caustic potash on the crude benzoin, I conclude that, under the circumstances above-detailed, it was separated into benzoic acid and two resins, of which the one is represented by $C_{40}\ H_{22}\ O_9$ (analyses 17 and 18), and the other by $C_{40}\ H_{30}\ O_7$ (analysis 19).

This second resin, by prolonged heating, gives off a volatile fluid, by which its constitution is gradually altered, becoming successively $C_{40}\ H_{30}\ O_8$, and $C_{40}\ H_{30}\ O_9$. The conformity of the analytical results with these formulæ is shown by the following tabular comparison:—

$C_{40}\ H_{30}\ O_7$ gives		Found analysis (19).	$C_{40}\ H_{30}\ O_8$ gives	Found analysis (22).	$C_{40}\ H_{30}\ O_9$ gives	Found analysis (21).
Carbon	73·99	74·03	72·25	71·80	70·58	70·61
Hydrogen	9·07	9·16	8·84	9·21	8·64	8·84
Oxygen	16·94	16·81	18·91	18·99	20·78	20·55
	100	100	100	100	100	100

To produce this change of constitution, it is only necessary that a carbo-hydrogen,

$C_{40} H_{30}$, should be given off, that is, a compound in which the elements are in the ratio of 4 to 3. Can the naphthoid fluid observed to pass off be such a compound?

That which is volatilized when the supposed resin $C_{40} H_{24} O_9$ is heated, cannot be of the same constitution, since the result is to increase the per centage of carbon, not to diminish it, as in the present case. (See analyses 7 to 13, and pp. 373 and 374.)

IV. *Action of Oxide of Lead on Resin of Benzoin.*

When a solution of acetate of lead in alcohol is poured into a similar solution of the resin of benzoin of commerce, a precipitate appears in comparatively inconsiderable quantity; and though both oxide of lead and resin be largely present, no further precipitate falls, unless fresh portions of the resinous solution be added.

This remark applies to the greater number of the resins belonging to our second group ($C_{40} H_{24 \pm x} O_y$). On the addition of caustic ammonia, however, a second and more copious precipitate is obtained.

1. *The precipitate which falls on the admixture of the two solutions.*

A portion of this salt being well washed, and afterwards dried at 250° FAHR., was subjected to analysis.

A. 6·10 grs. left 1·455 of oxide of lead, or 23·85 per cent.; and 12·91 grs. gave $\ddot{C} = 25{\cdot}42$, and $\dot{H} = 5{\cdot}89$ grs.

B. 4·625 grs. left 1·15 of oxide of lead, or 24·86 per cent.; and 10·535 grs. gave $\ddot{C} = 20{\cdot}68$ grs., and $\dot{H} = 4{\cdot}725$ grs.

These results are equal to

	A (23).	B (24).	
Carbon	54·45	54·28	40 atoms.
Hydrogen	5·07	4·99	22·4 atoms.
Oxygen	16·63	15·87	8·91 atoms.
Oxide of lead	23·85	24·86	1·05 atoms.
	100	100	

The formula $Pb\,O + C_{40} H_{22} O_9$, gives

		Per cent.
Carbon	3057·480	54·34
Hydrogen	274·549	4·88
Oxygen	900·000	16·10
Oxide of lead	1394·498	24·78
	5626·527	100

These calculated numbers agree very closely with those found by experiment, and would seem to justify us in adopting $C_{40} H_{22} O_9$, as the formula for the resin contained in this salt*. This, it will be observed, is also the formula for the resin precipitated, though in larger quantity, from the crude benzoin by caustic potash, and of which

* It is scarcely necessary to remark, that, if the resin employed contain any free benzoic acid, the precipitate here analysed would be mixed with benzoate of lead.

the experimental constitution is presented in the results of analyses 17 and 18, p. 376.

2. *The precipitate which falls on the addition of ammonia.*

A. Of this salt, washed and dried for several days at 200° FAHR.,

7·137 grs. left 2·957 of oxide of lead, or 41·41 per cent.

12·08 grs. gave $\ddot{C} = 18·01$, and $\dot{H} = 4·813$ grs., or per cent.,

	(25).	
Carbon	40·95	40 atoms.
Hydrogen	4·42	26·45 atoms.
Oxygen	13·22	9·88 atoms.
Oxide of lead	41·41	2·21 atoms.
	100	

The resin alone gives

Carbon	69·88
Hydrogen	7·54
Oxygen	22·58
	100

The oxide of lead is evidently not in atomic proportion, being thrown down probably in excess by the ammonia. But the resin indicates the formula $C_{40}\,H_{26}\,O_{10}$, which differs from any we have yet met with, in the analysis of the resin in its various states, as above-detailed, though other analyses, which I have not thought it necessary to insert, have given me results which would lead to a similar formula.

B. Of the salt last analysed, I decomposed a portion by boiling it with dilute muriatic acid, washed the resin well with water, dissolved it in alcohol, and dried it by a gentle heat, when

8·97 grs. gave $\ddot{C} = 22·79$, and $\dot{H} = 6·136$ grs.

Compared with analysis A. and with the formula $C_{40}\,H_{26}\,O_{10}$.

This result gives per cent.

	A (25).	B (26).	$C_{40}\,H_{26}\,O_{10}$ gives
Carbon	69·88	70·25	69·77
Hydrogen	7·54	7·60	7·40
Oxygen	22·58	22·15	22·83
	100	100	100

If implicit reliance could be placed on these analyses of the salts of lead, obtained directly and by the aid of ammonia, we should conclude that, by the action of oxide of lead, the resin of benzoin was separated into two resins represented respectively by $C_{40}\,H_{22}\,O_9$, and $C_{40}\,H_{26}\,O_{10}$. I am unwilling, however, myself to place implicit reliance upon them, knowing now how easily the resin undergoes decomposition by slight elevations of temperature; a fact of which I was not so well aware when these

analyses were made*. The entire subject of the action of alkalies and oxides on this resin is deserving of a complete revision, which it is my intention hereafter to undertake. The course and method of research, and the precautions to be adopted are clearly marked out by the experiments above-described, and I only leave the subject in its present incomplete state, because having made already nearly fifty analyses of this resin and its products, I may be permitted to turn my attention for a short time to some of the other members of this interesting natural family, on the constitution of which the above researches, though incomplete, tend to throw much light.

V. *On the rational Constitution of Resin of Benzoin.*

Benzoic acid is generally supposed† to exist ready formed in the resin of benzoin. It is obtained from the crude resin by sublimation, a gentle and uniform temperature being applied for several hours, when the acid forms beautiful crystals, amounting to about four per cent. of the weight of the resin employed. A quantity of water and of a volatile oil, having the odour of benzoin, is always (?) given off along with the acid, even when the operation is conducted in the most careful manner.

There are several circumstances which, though perhaps not decisive on the point, yet induce me to doubt whether the acid really exists ready formed, in any quantity at least, in the natural resin. A few of these I shall briefly state.

1. Heated alone at a temperature of 212° FAHR. benzoic acid is given off by the resin, it is also extracted by simple treatment with boiling water. But during this treatment the colourless resin always becomes coloured, and less fusible, and the brown shade deepens and the melting point rises, the longer it is heated even at this low temperature, till at length it becomes of a reddish-brown colour, and does not soften at a heat much above 212° FAHR. The mere removal of benzoic acid already existing in the resin, should not produce such a change in its physical characters.

It has been observed by BERZELIUS and other chemists, that when the resin of benzoin is heated, a volatile oil is given off, which, by the action of caustic potash, is transformed into benzoic acid. The removal of such an oil will account for the increased colour and diminished fusibility of the resin, while the agency of the atmosphere, when it is heated in the air, or of the elements of water when it is boiled in that liquid, or of the elements of the resin itself when it is heated alone, may produce to a certain extent the same effect as is caused more completely by the treatment with caustic potash‡. As a general observation, I have found that a deepening of the co-

* A mixture of the resin $C_{40}\ H_{26}\ O_{10}$ with benzoic acid ($C_{40}\ H_{14 \cdot 3}\ O_{8 \cdot 57}$), would give a formula approaching that of the resin contained in our first salt of lead, $C_{40}\ H_{22}\ O_{9}$.

† See LIEBIG's Chimie Organique, I. p. 241.

‡ This result of the action of caustic potash is not confined to the oil given off by benzoin. MÜLDER has observed, that the oil of cinnamon also ($C_{20}\ H_{11}\ O_2$) is transformed into benzoic acid by repeated distillation with caustic potash, and hence he has supposed that this oil may be a compound of benzyle ($C_{14}\ H_5\ O_2$) with a carbo-hydrogen (C H), since oil of cinnamon, $C_{20}\ H_{11}\ O_2 = C_{14}\ H_5\ O_2 + 6\,C\,H$. He has not satisfactorily

lour of a resin is a consequence of incipient decomposition, and is almost always attended by the evolution of a volatile oil.

2. Dilute solutions of carbonate of soda in the cold readily dissolve crystallized benzoic acid; but trituration, or even boiling with such solutions, does not deprive benzoin of the power of yielding this acid when subjected to heat. Concentrated solutions of the carbonated alkalies by boiling produce this effect, but they may act on the elements of the supposed oil as caustic potash does.

3. When boiled with caustic lime we have seen that a new resin is produced containing much more hydrogen; the same effect follows, and to a greater extent, by treatment with caustic potash even in the cold. This effect is most readily explained by supposing a decomposition to have taken place, by which a substance containing less hydrogen (benzoic acid) is separated, and one containing more is formed, or separated along with it.

4. It may be stated, as in some measure corroborating the above arguments, that when the resin of dragon's blood is heated for a length of time at a temperature at which it barely fuses, it gives off benzoic acid, water, and a reddish volatile oil, but is at the same time itself so much decomposed, that though retaining its red colour it becomes in a great measure insoluble in alcohol.

These reasons do not appear to me to *decide* that no benzoic acid exists in the benzoin resin of commerce, but they render it probable, I think, that very little does so exist, at *least in a free state*, in the white varieties. The brown varieties appear to be already in some measure decomposed, and hence their colour, and the presence probably of some free acid; but all the varieties undergo further decomposition and yield more acid, when exposed to a high temperature or to the action of bases, which by their affinities *dispose* the elements to arrange themselves so as to liberate benzoic acid.

But admitting this explanation, the question remains, In what state do the elements of benzoic acid exist in the resin? Is benzoic acid present as such, but in combination with the resins, which by the action of alkalies and oxides are eliminated along with it? Are the resins analogous to the fatty bodies, and do the bases act upon each family of substances in an analogous manner, liberating from the former an oil, the analogue of glycerine (hydrated oxide of glyceryle $= C_6\ H_7\ O_5 + H\ O$) and two resins, the analogues of the oleic and stearic acids; and is this oil again, by a secondary action of the bases, converted into benzoic or some similar acid, and one or more other as yet undetected compounds? Or do the resins consist of this or an analogous acid ready formed and directly combined with one or more basic resins? Though I feel

shown, however, that no other substance is formed at the same time as the benzoic acid. BERZ. Årsberättelse, 1837, p. 269.

It is interesting to observe, that in $C_{20}\ H_{11}\ O_2$, or $C_{40}\ H_{22}\ O_4$, we have the same ratio of the carbon to the hydrogen as in our resin $C_{40}\ H_{22}\ O_9$.

that the state of our knowledge does not justify me as yet in forming more than a conjecture on the subject, yet at present I am inclined to regard the former opinion as much the more probable. In future papers, I hope to be able to place the question in a more satisfactory point of view, by the aid of other experimental researches, which I shall then have had an opportunity of bringing before the Society.

In favour of the view of the constitution of the fragrant resins* above preferred, I would direct attention to the researches of FREMY, into the constitution of the balsams of Peru and Tolu†, in which he has detected an oily liquid (cinnameine = $C_{54}\ H_{26}\ O_8$), convertible by the action of caustic potash into cinnamic acid = $C_{18}\ H_8\ O_4$, and by chlorine, among other products, into chloride of benzyle, which water, as is well known, converts into benzoic acid. This action of potash on cinnameine he compares to that of the same base on oleine; and he considers it highly probable that the resin of benzoin, while in the balsamic state, contains an oily fluid, which by potash is convertible into benzoic acid.

FREMY has also analysed the resin of benzoin in conjunction with those extracted by him from the balsams of Peru and Tolu, and that which is obtained by the action of sulphuric acid on cinnameine.

His comparative results are as follow:—

	From balsam of Peru.	From balsam of Tolu.	From cinnameine.	Resin of benzoin.
Carbon	71·82	70·8	71·9	71·2
Hydrogen	6·78	6·1	6·5	6·5
Oxygen	21·40	23·1	21·1	22·3
	100	100	100	100

The several resins he concludes to be identical, and represents them by the formula $C_{54}\ H_{30}\ O_{12}$, which nearly coincides with our formula $C_{40}\ H_{22}\ O_9$, and gives carbon 72·4, hydrogen 6·5, and oxygen 21·1 per cent.

The above results, however, are too discordant to justify the conclusion that the resins are identical. Besides, he only gives one analysis of each resin, and describes them, in consequence of the instability of the compounds, only as tolerable approximations‡. That such is the case, indeed, is evident from his adoption of a common formula, which requires four-tenths (0·4) per cent. more hydrogen than was obtained by analysis in one of his experiments. In regard to his analysis of the resin of benzoin, it approaches nearest to No. 1. of the series given in the present paper, and may be considered in so far to confirm the statements I have had occasion to make, in regard to the slight circumstances by which the constitution of the resin may be made to vary, and the difficulty of admitting the opinion that the benzoic acid exists in it ready formed.

The portion analysed by FREMY gave only 6·5 per cent. of hydrogen, and could not

* Those represented by the formula $C_{40}\ H_{24 \pm x}\ O_y$.

† Annales de Chimie et de Physique, LXX. p. 180.

‡ See his memoir, p. 204.

therefore have been deprived of all the benzoic acid it was capable of yielding; though he states that it had been purified after the method of UNVERDORBEN (see above, analyses 4, 5, 6, and 11, 12, 13.).

General Results in regard to the Resin of Benzoin.

From the experiments detailed in the present paper it appears probable,

1. That the colourless resin of benzoin is represented very approximately by the formula $C_{40}\ H_{22}\ O_9$.

2. That by the action of heat, of boiling water, or of dilute solutions of the carbonated alkalies, it is partially decomposed, giving off a volatile oil, a little water and benzoic acid, and acquires a composition represented approximately by $C_{40}\ H_{23}\ O_9$, and $C_{40}\ H_{24}\ O_9$.

3. That by the action of concentrated solutions of the carbonated alkalies, at a boiling temperature, and of quicklime in boiling water, it is resolved into benzoic acid, into one resin, $C_{40}\ H_{24}\ O_8$, which does not dissolve, and into another (the resin C. of UNVERDORBEN*?) which the salt of lime or of potash dissolves, and which is represented by $C_{40}\ H_{30}\ O_7$.

4. That caustic potash in like manner decomposes the crude resin, throwing down from the alcoholic solution a potash salt, which consists chiefly of a compound of the alkali with a resin represented approximately by $C_{40}\ H_{22}\ O_9$, but which is of a darker colour and is more sparingly soluble than the natural resin, to which the same formula has been ascribed. The supernatant solution, now of a darker colour, contains the second resin, $C_{40}\ H_{30}\ O_7$, already obtained by the action of the carbonated alkalies.

5. That by oxide of lead an analogous change is produced upon the crude resin; the precipitate which falls, on mixing the alcoholic solutions of the resin and of acetate of lead, containing by experiment $C_{40}\ H_{22}\ O_9$, and that which is thrown down by the subsequent addition of caustic ammonia, a resin $C_{40}\ H_{26}\ O_{10}$†.

6. That all these resins are decomposed more or less easily, giving off volatile matters at a temperature much below that at which they melt, and that the results of different analyses of the same portions of resin are thus liable to be modified to a considerable extent.

It was my intention to have included in the present paper some new analyses of the resin of dragon's blood, already examined in the first part of these researches, and of the new resins produced by the action of quicklime and of oxide of lead on the several

* THOMSON's Organic Chemistry (1838), p. 542.

† I have not adverted to the *apparent* difference between this resin and the resin $C_{40}\ H_{24}\ O_8$, that namely of the elements of two atoms of water only. I am unwilling to adopt the opinion that any of the resins contain water as a constituent, till we have some distinct facts on which to rest; but there can be no difficulty in allowing that, under certain circumstances, one resin may be transformed into another by *assimilating* the elements of one or more atoms of water.

varieties of the dragon's blood of commerce. But my remarks on the resin of benzoin have extended so much, that I think it better to reserve them for a future opportunity; I may merely state generally, that while the formula assigned to the resin contained in the lump dragon's blood is $C_{40} H_{21} O_8$, and to the drop variety after long heating at 300° FAHR, $C_{40} H_{20} O_8$, the same varieties yield by the action of quicklime and of oxide of lead, among other products two resins, represented approximately by $C_{40} H_{20} O_{10}$, and $C_{40} H_{20} O_{12}$?; that the resin of assafœtida, which in Part IV. is expressed by $C_{40} H_{26} O_{10}$, gives with oxide of lead one resin, $C_{40} H_{23} O_{13}$; that the resin of jalap $= C_{40} H_{34} O_{18}$, in like manner with oxide of lead, gives a new resin, $C_{40} H_{34} O_{20}$, and the resin of guiacum $C_{40} H_{23} O_{10}$, one represented by the formula $C_{40} H_{21} O_{11}$. The experiments from which these and other interesting formulæ are deduced, I shall have the honour of laying before the Society on a future occasion.

Having in the former papers on this subject, and in the commencement of the present, established certain approximate *irrational* formulæ for numerous resins, we have by these later results and observations been led considerably further in advance, and into a new portion of the field of inquiry.

They have opened up the question as to the *rational* constitution of the resins, and have enabled us to hazard a conjecture, in regard to what that constitution may really be.

We have seen reason from the irrational constitution of the resins to divide them into two groups characterized by unlike general formulæ, and we have observed a general analogy also in physical characters, among the members of each group. A comparison of the effect of bases on these several resins seems to confirm the propriety of this division, since the analyses of the salts of the resins, of which colophony is the type, *appear* to show that in combining with bases they undergo no change, or if any, only in regard to the number of atoms of hydrogen, and this is doubtful; while all those resins, to the salts of which reference has been made in the present paper, indicate an important metamorphosis or decomposition as the result of the action of bases. This distinction, if general, is a very wide one, and must arise from the arrangement of the constituent elements in two ways very unlike each other. Too much weight, however, is not to be attached to these apparent distinctions, as they may vanish on further investigation.

Durham, June 3, 1840.